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<b>(21) International Application Number:</b> PCT/US97/19411 <b>(22) International Filing Date:</b> 29 October 1997 (29.10.97)  <b>(30) Priority Data:</b> 08/743,007                      1 November 1996 (01.11.96)                      US  <b>(71) Applicant:</b> CLEARWATER, INC. [US/US]; 5605 Grand Avenue, Pittsburgh, PA 15225 (US).  <b>(72) Inventors:</b> SMITH, Kevin, W.; 103 Fairway Road, McMurray, PA 15317 (US). PERSINSKI, Leonard, J.; 340 Orchard Spring Road, Pittsburgh, PA 15220 (US).  <b>(74) Agent:</b> KRAYER, William, L.; 241 Merion Drive, Pittsburgh, PA 15228 (US).		<b>(81) Designated States:</b> CA, NO, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> PREPARATION OF HYDROCARBON GELS FROM FERRIC SOURCES, POLYCARBOXYLIC ACID COMPOUNDS, AND OPTIONAL AMINES, IN COMBINATION WITH PHOSPHATE ESTERS  <b>(57) Abstract</b>  This invention relates to improved hydrocarbon gels which find use in the fracturing of petroleum producing formations. In particular it relates to the use of a define class of gelling agents for hydrocarbons which provide excellent results in such fracturing. The gelling agents comprise combinations of (1) selected orthophosphate esters and (2) a composition comprising a source of ferric ions, an amine, and a polycarboxylic acid or salt thereof.		

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**PREPARATION OF HYDROCARBON GELS FROM FERRIC SOURCES,  
POLYCARBOXYLIC ACID COMPOUNDS, AND OPTIONAL AMINES,  
IN COMBINATION WITH PHOSPHATE ESTERS**

5       **Related Application**

10       This application is a continuation-in-part of (a) our  
US Patent Application SN 08/592,592 filed January 26,  
1996 and (b) our US Patent Application SN 08/580,171  
filed December 28, 1995, both of which are  
continuations-in-part of US Patent Application SN  
08/360,438 filed December 21, 1994, now abandoned,  
which is a division of Application Serial Number  
08/209,266 now US Patent 5,417,287.

15

**Technical Field**

20       This invention relates to improved hydrocarbon gels  
which find use in petroleum producing formation  
fracturing. In particular it relates to the use of a  
defined class of gelling agents for hydrocarbons which  
provide excellent results in such fracturing. The  
gelling agents are combinations of (A) selected  
orthophosphate esters and (B) sources of iron mixed  
25       optionally with ammonium sources or alkyl or alkanol  
amines, and further with polycarboxylic acids or their  
alkali metal salts. The mixtures (B) may be reacted  
to form such compounds as ferric ammonium citrate  
and/or lower alkyl or alkanol derivatives thereof.

30

**Background of the Invention**

35       The development of the use of gelled hydrocarbons as  
fracturing fluids is reviewed by Weldon M. Harms in a  
chapter entitled "Application of Chemistry in Oil and  
Gas Well Fracturing", at pages 59-60 of the book "Oil-  
Field Chemistry (ACS Symposium #396 - 1988)" published

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by the American Chemical Society in 1989. The basic technique of formation fracturing involves the injection of a fracturing fluid down the well bore, which is usually cemented in place and at least 0.3 mile long, and then through horizontal holes in the steel pipe, or casing, of the well, to obtain access to the subterranean formation. The fracturing fluid is under high pressure and must be able to survive the severe shear forces caused when flow is forced through the casing perforations of perhaps  $\frac{1}{8}$  to  $\frac{1}{4}$  inch in diameter, as well as the shear forces encountered at the leading edge of the fracture. Whatever chemical additives are used to influence viscosity, induce gel formation, stabilize against resident chemicals, pH or temperature conditions in the formation, inhibit scale formation or corrosion, or inhibit paraffin deposition, for example, must also be able to withstand the shear forces and other inhospitable conditions of use. Most commonly available liquids typically are viscosified before they are particularly effective in carrying the large quantities of proppants widely used in the fracturing process.

When hydrocarbons are used in the fracturing process, they are commonly treated to increase their viscosity. As reviewed by Harms, an early viscosifying agent was napalm, an aluminum soap of fatty acids. Aluminum salts of orthophosphate esters were introduced in the late 1960's, followed by the suggestion of the use of  $\text{Fe}_3\text{O}_4$  for combination with the orthophosphate esters, in **Monroe** US Patent 3,505,374. While many other combinations of metals and other materials have been suggested as viscosifying agents, aluminum crosslinked orthophosphate esters are still, according to Harms, the most widely used.

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5 The aluminum compounds present problems, however,  
particularly where any significant amount of water is  
present. They generally will not satisfactorily  
perform the desired crosslinking function in the  
presence of more than about 1200 ppm of water, nor  
where the pH is outside a relatively narrow range.  
Moreover, an inadvertent excess of aluminum compound  
treatment is detrimental to the desired performance  
10 because the aluminum compound itself adversely affects  
the pH. The iron provided by ferric salts as in the  
present invention and described in the parent  
applications hereof and in related US Patent  
5,417,287, on the contrary, permits operation in wider  
15 pH ranges.

In describing a gel which can be used as a pig in a  
pipeline, **Jaggard** et al in US Patent 4,003,393 recite  
the possibility of iron as one of a number of metals  
20 to combine with a class of aliphatic substituted  
orthophosphoric esters. No other qualifiers are used  
to describe the iron, however.

25 In US Patent 4,153,649, **Griffin** proposes reacting a  
pentavalent phosphorous compound with a class of  
hydroxy ethers before employing the metal salt. Among  
the metal salts he uses is ferric nitrate, but he  
further requires a "separate source of base" to be  
used with the hydroxy ether modified phosphates, as  
30 spelled out in column 4, lines 55-58 and column 11,  
lines 37-68. In the latter passage, the ferric  
nitrate is combined with ethylene diamine tetraacetic  
acid, a well-known chelating agent.

35 **Monroe**, in US Patent 3,505,374, uses a gelling agent

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for hydrocarbons characterized as a ferroso-ferric salt of an alkyl oleyl diester of orthophosphoric mono acid. The iron compound is further described as magnetite, or  $\text{Fe}_3\text{O}_4$ . He suggests this combination for fracturing subterranean oil-bearing formations, but says none of the "other oxidized forms of iron including ferrous and ferric oxides and hydroxides, chlorides, sulfates and nitrates" (col 3, lines 2-4) yielded a gel as obtained with the magnetite.

**Burnham**, in US Patent **4,200,540**, describes a large class of phosphates and phosphate esters which he mixes with aluminum salts, aluminates and aluminum metal. He chooses combinations of the materials as a function of various down-hole temperatures. No mention is made of iron salts; the reference is cited mainly for its comprehensive description of the phosphates deemed to be useful. See also **Burnham's** US Patent **4,316,810**.

In United States Patent 5,514,645, McCabe utilizes a reaction product of an inorganic iron or aluminum salt with a  $\text{C}_{8-18}$  surface active amine to mix with a phosphate ester in a hydrocarbon to viscosify it as a fracturing medium. He does not include a polycarboxylic acid, however, as in the present continuation-in-part application.

A reaction product of citric acid and monoethanolamine is used with phosphoric acid in treating sandstone formations by **Young et al** in US Patent **4,605,068**. The treatment has nothing to do with gelling hydrocarbons, however.

**Summary of the Invention**

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We have found that ferric salts can be very advantageously used in the gelling of hydrocarbons, particularly for use in formation fracturing, rather than aluminum compounds, for combination with orthophosphate esters. The present continuation-in-part application is concerned specifically with mixtures of ferric salts with amines and polycarboxylic acids, and also with reaction products of polycarboxylic acid in which the polycarboxylic acid moiety has from 2-12 carbon atoms and/or lower alkyl and alkanol derivatives thereof such as, to name a few examples, ferric butanol amine citrate, ferric isopropanolamine citrate, ferric triethanolamine succinate, and ferric dibutanolamine tartrate, i.e. where each alkyl or alkanol moiety may have up to six (6) carbons..

The ferric salts have the advantage that they can be used in the presence of large amounts of water, such as up to 20%. One of the advantages of fracturing with hydrocarbon gels is that some formations may tend to imbibe large quantities of water, while others are water-sensitive and will swell inordinately if water is introduced; our invention permits one to use a hydrocarbon gel in areas where water may cause trouble not only with the formation itself, but with the fracturing agent or the gelling agent. Also, ferric salts are not adversely affected by commonly used alcohols, such as methanol and isopropanol. In addition, they can be used in broad ranges of pH, yet the linkages formed can still be broken with gel breaking additives conventionally used for that purpose. In addition, ferric salts such as ferric sulfate and the more complex ferric salts and other ferric iron sources we use crosslink rapidly and can

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be made to link even more rapidly with the use of surfactants and/or alkaline or caustic agents such as potassium hydroxide, triethylamine, and triethanolamine.

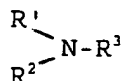
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When dissolved in a hydrocarbon such as gasoline, diesel oil, crude oil, or kerosene, the ferric salt in combination with orthophosphate esters as defined below will cause the hydrocarbon to gel. The gel is generally stable to heat, and the degree of gelling can be controlled by the concentration of orthophosphate ester in the fluid. As further described herein, ferric ammonium (or alkyl or alkanol amine) citrate or other polycarboxylate will generate gels of enhanced strength and temperature resistance. In addition, the apparent chelation of the iron by the polycarboxylic acid moiety inhibits the precipitation of the iron in the form of ferric hydroxide.

20

Thus our invention includes a method of fracturing a subterranean formation comprising adding to a hydrocarbon liquid to be used as a fracturing fluid (a) about 0.3% to about 1.5% by weight, based on the hydrocarbon liquid, of an organic phosphate of the formula  $\text{HPO}_4\text{RR}'$  where R is a straight or branch chain alkyl, aryl, alkoxy or alkaryo group having from 6 to about 18 carbon atoms and R' is hydrogen or an aryl, alkaryl, alkoxy or alkyl group having from 1 to about 18 carbon atoms, and (b) a composition comprising (i) a source of ferric iron in an amount effective to form a gel with the phosphate ester in the hydrocarbon (ii) an amine having the general formula

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where R' is  $(\text{CH}_2)_{2-6}\text{R}^4$ , R<sup>4</sup> is H or OH, R<sup>2</sup> is  $(\text{CH}_2)_{0-6}\text{H}$  or  $(\text{CH}_2)_{2-4}\text{OH}$ ,

R<sup>3</sup> is R<sup>2</sup> or  $(\text{CH}_2)_{2-6}\text{N} \begin{smallmatrix} \text{R}^2 \\ \text{R}^5 \end{smallmatrix}$  and R<sup>5</sup> is R<sup>2</sup> or  $-(\text{CH}_2)_{2-6}\text{N} \begin{smallmatrix} \text{R}^2 \\ \text{R}^2 \end{smallmatrix}$

and (iii) a polycarboxylic acid or an alkali metal salt thereof, having from 2-12 carbon atoms and up to three amine groups. The amounts and preferred methods of addition of the amine and polycarboxylic acid are discussed below.

#### Detailed Description of the Invention

The phosphate ester which we use is advantageously added first and mixed with the Diesel fuel or other hydrocarbon to be used as the fracturing agent, generally in amounts from about 0.3% to about 1.5% by weight, based on the total. Then the ferric salt or lower alkyl or alkanol derivative, specifically the ferric ammonium citrate (or other composition comprising ferric salt, amine (if used), and di- tri- or tetra- or pentacarboxylate having 2-12 carbon atoms and up to three amine groups) is added in amounts to provide preferably in the range of about 0.25 mole of ferric iron for each mole of phosphate or phosphate ester to about 2 moles of ferric iron for each mole of phosphate or phosphate ester. In this manner, the process materials can be prepared more or less continuously, as opposed to the batch approach sometimes used in the past. More broadly we may use any amount of ferric salt such as ferric ammonium lower alkyl or alkanolamine polycarboxylate which is effective to make a gel with the phosphate ester. This will be accomplished at about 0.1 to about 2.5 mole of ferric iron for each mole of phosphate ester,

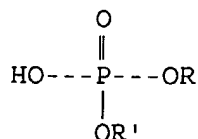
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preferably 0.8:1 to 1.2:1. Very small amounts (for example less than 0.1 mole/mole of phosphate ester) of ferric ammonium citrate or its lower alkyl or alkanol derivatives or other ferric containing composition as described herein will have at least some gelling effect; amounts over 2 or 2.5 moles/mole of phosphate will generally be superfluous. The choice of ratios will vary with the circumstances and the objectives of the practitioner.

We have also found that surfactants have the effect of decreasing the time for crosslinking. Generally, in the absence of a surfactant, our combination of materials will crosslink in about two minutes at room temperature; when a surfactant is used also, this time is significantly reduced, and in the presence of our preferred class of surfactants, it is reduced to the neighborhood of twenty seconds, as determined by viscosity tests. About 0.1% to about 10% (based on the gelling agent) of surfactant is frequently advantageous also.

#### The Phosphate Ester

The phosphate derivatives we use are described in the literature as orthophosphate esters. They are similar to those used by **Burnham** in US Patents 4,200,540 and 4,316,810. **Griffin** US Patents 4,174,283 and 4,153,649, and **Harris** et al in US Patent 4,622,155, having the structural formula



where R is a straight or branched chain alkyl, aryl, alkoxy, or alkaryl group having about 6 to about 18

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carbon atoms and R' is hydrogen or an aryl, alkaryl, alkoxy, or alkyl group having up to about 18 carbon atoms. This structural formula will be referred to elsewhere herein as  $\text{HPO}_4\text{RR}'$ .

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### The Iron Sources

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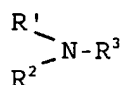
Our preferred original source of the ferric ion is ferric sulfate, but any organic or inorganic ferric salt may be used, and it is apparent that the sulfate or other anion is not important in our invention. In the discussion throughout, it should be understood that where ferric sulfate is mentioned, it could as well be any other ferric salt which will provide the desired ferric ion under the conditions, particularly of solubility, described. Typically we work first with a 50% solution of ferric sulfate.

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### The Amine

As indicated above, the amine may be any amine having the general formula

25



30

where R' is  $(\text{CH}_2)_{2-6}\text{R}^4$ , R<sup>4</sup> is H or OH, R<sup>2</sup> is  $(\text{CH}_2)_{0-6}\text{H}$  or  $(\text{CH}_2)_{2-4}\text{OH}$ ,

R<sup>3</sup> is R<sup>2</sup> or  $(\text{CH}_2)_{2-6}\text{N} \begin{array}{l} \diagup \text{R}^2 \\ \diagdown \text{R}^5 \end{array}$  and R<sup>5</sup> is R<sup>2</sup> or  $-(\text{CH}_2)_{2-6}\text{N} \begin{array}{l} \diagup \text{R}^2 \\ \diagdown \text{R}^2 \end{array}$

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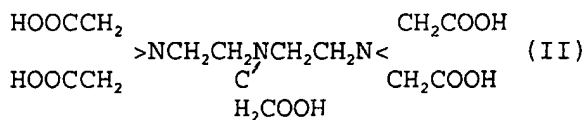
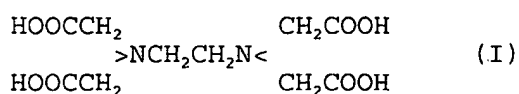
As is seen from the formula, the amine need not be a polyamine and if a monoamine it may be a primary, secondary or tertiary amine. The amine may be a primary, secondary or tertiary amine having at least

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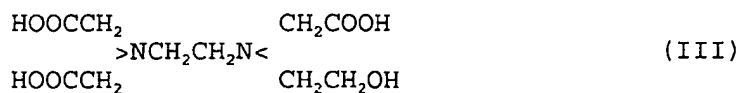
one substituent alkyl or terminal (OH on the terminus) alkanol group of two to six carbon atoms, the other two substituents being alkyl or terminal (OH on the terminus) alkanol groups having 0-6 carbons. If it is a polyamine, the connecting alkyl groups have two to six carbon atoms and the remaining positions on the nitrogens are filled by alkyl groups of 0-6 carbons or terminal alkanol groups of 2-6 carbon atoms.

### The Polycarboxylic Acid

Instead of citric acid, one may use any polycarboxylic acid having from 2 to 12 carbon atoms and up to three amine groups. Suitable examples are oxalic acid, succinic acid, maleic or fumaric acid, tartaric acid, suberic, malonic, glutaric, adipic, pimelic, azeleic, or sebacic acid, nitrilitriacetic acid, ethylene diamine tetraacetic acid (EDTA), phthalic acid, isophthalic acid, and terephthalic acid. The polycarboxylic acids include compounds of the formulas



or



### The Proportions

In making the iron-containing compound for use with the phosphate ester, the carboxylic acid containing

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compound (typically an alkali metal salt thereof) is added to the combined iron/ammonium, alkyl or alkanol amine as stated above with respect to the addition of citric acid. For effective gelling of the hydrocarbon, the phosphate ester is present in the hydrocarbon in an amount from 0.3 to 1.5% by weight. It is generally most relevant to base the ferric iron content on the phosphate ester, and as little as 0.1 mole of ferric iron per mole of phosphate ester can bake a gel; however, we prefer about 0.25 to 2 moles ferric iron per mole of phosphate ester. While 0.1 to 2.5 moles of ferric iron per mole of phosphate ester may be used, amounts greater than 2.5 moles of ferric iron per mole of phosphate ester are generally superfluous. The amine is optional but frequently beneficial. If used, it may be present in an amount up to ten times the amount by weight of the ferric iron. More may be used, but such amounts will generally be superfluous. The polycarboxylic acid or alkali metal salt should be used in amounts from 10:1 to 1:10 weight/weight of the ferric iron. Again, amounts higher than 10:1 may be used but will generally be superfluous; amounts lower than 1:10 may also be used with commensurately small effect.

In the fracturing fluid, the iron from the ferric sulfate or other ferric salt such as ferric ammonium citrate, ferric butyl amine citrate, ferric isopropylamine citrate or ferric trialkanol tartrate, or from the unreacted ferric compound containing composition, including a polycarboxylic acid, forms linkages with the available oxygen, generally in more than one phosphate group, thus forming small chains which cause the hydrocarbon to gel.

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It has been demonstrated in the laboratory that our invention may be used to form hydrocarbon gels, and that the gels can be broken in a manner familiar to persons who work with hydrocarbon gels in the field such as by the addition of common alkaline materials. In the following examples, the procedure was to employ a laboratory Waring blender with a voltage regulator set at 30. 300 ml of Diesel oil was placed in the blender and the power turned on. The phosphate ester preparation was first added and after it was blended, the ferric salt solution was introduced by pipette. The time was recorded from the initial introduction of the ferric compound to the gel point, determined by a concave shape of the material in the blender.

Blending was continued to determine the time required to reach maximum gel, which was estimated to be the first sign of conversion of the shape of the material to convex instead of concave. The blending was then stopped and the material transferred to a sample container, observing the consistency of the gel. Brookfield viscosity readings were then taken as shown in the Table I.

In the examples below, Composition M is about two-thirds phosphate ester of the above formula  $\text{HPO}_4\text{RR}'$ , together with triethanolamine, and solvent. Composition L contains about two-thirds phosphate ester  $\text{HPO}_4\text{RR}'$ , together with triethylamine, and high flash aliphatic solvent. Composition K is two-thirds of the same phosphate ester and 15.5g 45%KOH, also with a solvent. Composition F contains about 27% ferric sulfate, together with ethylene glycol, mixed surfactants, triethanolamine, and water. In each case, the amounts of composition M shown were added

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first to the Diesel oil and blended; then the amount shown of Composition F was added and blended. Results are presented in Table I.

5

Table I

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Ex	M	F	X-link	Invers	Spindl	5min	30min	60min
1	3ml	3ml	20 sec	30 sec	#3	2500	-	3890
2	3ml	3ml	20 sec	30 sec	#3	2300	-	3460
3	3ml	3ml	25 sec	35 sec	#3	2375	-	3400
4	3ml	3ml	30 sec	60 sec	#4	6360	11000	13800
5	3ml	3ml	30 sec	55 sec	#4	7320	12300	13500
6	3ml	3ml	45 sec	none at 180 sec				
7	2ml	2ml	60 sec	150 sec	#4	-	-	-
8	3ml*	3ml	20 sec	55 sec	#3	10000 <sup>†</sup>	-	13000 <sup>†</sup>
9	6ml*	3ml	15 sec	30 sec	#4	-	-	21500 <sup>†</sup>
10	2ml <sup>§</sup>	3ml	20 sec	35 sec	#4	13650 <sup>†</sup>	-	13850 <sup>†</sup>

\* Composition L used instead of M  
<sup>†</sup> Composition K used instead of M  
<sup>§</sup> rotation at 10 rpm

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Persons skilled in the art will recognize from Table I that the formulations make excellent gels.

In a separate experiment, it was shown that the order of addition of the phosphate ester solution (sometimes herein called the gellant) and the ferric sulfate (or other iron salt such as ferric ammonium citrate) component (activator) is not important. In this experiment, 6.16g deionized water and 1.3g ferric sulfate were added to 85.95g Diesel oil and mixed with the blender; then 0.4 ml of phosphate esters of the formula  $\text{HPO}_4\text{RR}'$  was added and inversion took place in about one minute.

The data in Table II demonstrate that our hydrocarbon gel former will operate in the presence of significant amounts of water; indeed the viscosity increases with increasing amounts of water. In this experiment, an initial mixture was made as above with 4g of gellant and 10g of activator in about 250g of Diesel oil. Water was then added incrementally and the viscosity measured immediately.

Table II

	Cumulative Water, %	Viscosity (511 sec <sup>-1</sup> )
	0.65%	1cp
	1.27%	6cp
	2.16%	12cp
	2.78%	19cp
	3.50%	26cp
	4.18%	29cp
	5.06%	30cp
	6.17%	*
	7.58%	*
	8.38%	*
	10.41%	*
	14.78%	*
	20.2 %	*
*	Dial bouncing and unreadable; excellent lipping gel observed.	



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Additional tests were made as shown in Table III, which records the viscosities achieved by various combinations within our invention.

Table III

	ml M	ml F	cps	ml other	comment
5	3	3	13,800		
	3	3	13,500		
	2	2	(bouncing dial)		
10	a	3	13,000		
	b	3	21,500	6TEA*	
	c	3	13,900	2KOH	
	3	3	15,000		
	3	3	16,000		
15	d	3	5,800	low acid value PE	
	e	3	9,400	high acid value PE	
	f	3	20,800	KOH	
	g	3	11,300	1/2KOH	
	3	3	7,000	1/2KOH	
20	3	3	8,600	no TEA in F	
	3	3	8,700	KOH in M; no TEA in F	
	3	3	14,500	KOH in M; no TEA	
	3	3	13,400		
25	3	3	-	4400 cps @ 20 rpm	
	i	3	9,300		
	j	3	20,400		
	2 ml	3	12,700		
	2 ml	1.5	8,300		
30	k	1.5	10,000		
	l	1.5	12,500	2 ph est; KOH; 1.5 Fe	
	3	3	14,700		
	m	3	20,000		
	3	3	23,000	0.25g Na <sub>2</sub> CO <sub>3</sub>	
35	n	3	21,000		
	o	3	18,400	0.25g Na <sub>2</sub> CO <sub>3</sub>	
	3	3	19,500	0.5g CaCl <sub>2</sub>	
	p	3	13,800	0.5g CaCl <sub>2</sub>	
	2	3	7,000		
40	q	3	11,600		
	r	3	12,100		
	3	3	10,500		
	3	3	10,500	Fe Citrate	
	3	3	9,700		
45	3	3	6,800	Fe Citrate	
	u	3	8,200		
	v	3	18,400	Na <sub>2</sub> CO <sub>3</sub>	
	w	3	21,000	Na <sub>2</sub> CO <sub>3</sub>	
	x	3	10,000		
50	y	3	11,000		
	aa	2	6,700		
	bb	1	780		
	cc	4	12,300		
	dd	3	13,000		
55	ee	4	12,200		
	ff	5	12,000		
	gg	6	11,500		
	hh	7	12,300		
	ii	9	11,500		
60	jj	11	11,400		
	kk	13	13,300		
	ll	17	11,800		
	mm	3	10,900		
	nn	3	14,700		
65	oo	2	14,900		
	pp	4	14,900		
	qq	6	12,500		
	rr	8	12,700		
	ss	11	10,400		
70	tt	15	7,600		

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In Table III, the following notes apply to the column headed "ml Other":

5	a	triethylamine with phosphate ester of M -- 3 ml
	b	triethylamine with phosphate ester of M -- 6 ml
	c	KOH with phosphate ester of M -- 2 ml
	d	triethanolamine with varied phosphate ester -- 3 ml
	e	triethanolamine with varied phosphate ester -- 3 ml
	f	KOH with phosphate ester of M -- 3 ml
10	g	same as f with half as much KOH -- 3 ml
	h	same as g with half as much KOH -- 3 ml
	i, m, n, o, p	KOH with phosphate ester of M -- 3 ml
	k, l	KOH with phosphate ester of M -- 2 ml
	q, r, s	KOH with varied phosphate ester -- 2 ml
15	t, u, v, w, x, y	no alkali; phosphate ester of M -- 3 ml
	aa	3 ml non-neut phosphate ester; 2ml F
	bb	3 ml non-neut phosphate ester; 1 ml F
	cc	3 ml non-neut phosphate ester; 4 ml F
	dd	3 ml KOH-treated phosphate ester; 3 ml F
20	ee	3 ml KOH-treated phosphate ester; 4 ml F
	ff	3 ml KOH-treated phosphate ester; 5 ml F
	gg	3 ml KOH-treated phosphate ester; 6 ml F
	hh	3 ml KOH-treated phosphate ester; 7 ml F
	ii	3 ml KOH-treated phosphate ester; 9 ml F
25	jj	3 ml KOH-treated phosphate ester; 11 ml F
	kk	3 ml KOH-treated phosphate ester; 13 ml F
	ll	3 ml KOH-treated phosphate ester; 17 ml F
	mm	3 ml non-neut phosphate ester; 3 ml F
	nn	3 ml non-neut phosphate ester; 2 ml F
30	oo	3 ml M; 4 ml F
	pp	3 ml M; 6 ml F
	qq	3 ml M; 8 ml F
	rr	3 ml M; 11 ml F
35	ss	3 ml M; 15 ml F

From the above table III, it is apparent that a broad range of ferric salts, neutralizing agents, and other additives such as breakers, and other materials are not detrimental to the gelling abilities of our invention.

In the following Table IV, ferric salts as shown were used in combination with a standard 3 ml concentration of phosphate ester solution, some with KOH and some without, in 300 ml oil. The viscosity was measured with a #4 spindle at 10 rpm unless otherwise noted.

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Table IV

	<u>Iron salt</u>	<u>ml Fe</u>	<u>Viscosity</u>	<u>Comment</u>
	Fe Citrate	3	6,800	
	Fe Citrate	1	8,800	
5	Fe Citrate	3	16,700	
	Fe Citrate	3	7,000+	
	Fe Citrate	2	8,000	
	Fe Citrate	2.5	3,300	#3 spnd1; 10rpm
	Fe Citrate	2.5	3,200	"
10	Fe Citrate	2.5	3,200	"
	Fe Citrate	2.5	2,700	"
	Fe Amm Sulf	1	13,000	
	Fe Amm Sulf	1	3,500	(20 rpm)
	Fe Amm Sulf	1.5	14,700	
15	Fe Amm Sulf	1.5	15,000	
	Fe Chloride	3	6,200	
	Fe Chloride	2	7,600	
	Fe Sulfate	1	9,700	
	Fe Sulfate	1.5	14,000	
20	Fe Sulfate	1	7,000	
	Fe Amm Citrate	3	12,000	
	Fe Gluconate	3	4,600	

25 A further series of tests was conducted specifically  
 with ferric ammonium citrate, ferric butylamine  
 citrate, and ferric isopropylamine citrate. Ferric  
 ammonium citrate was made according to the procedures  
 described by Kruse and Mounce in US Patent 2,644,828,  
 which is hereby incorporated herein by reference in  
 30 its entirety. Because the structural formula of this  
 composition is uncertain, i.e. the amount of NH<sub>3</sub>  
 appears to vary with the color and physical form (see  
 the listing of Ammonium Ferric Citrate in the Merck  
 Index, Eighth Edition), we intend to include within  
 35 the definition of ferric ammonium citrate any of the  
 compositions contemplated within the aforesaid Kruse  
 et al '828 patent. Both brown and green crystalline  
 forms are described in the '828 patent. Generally,  
 the procedure we followed was to form a solution of  
 40 ammonium hydroxide and ferric sulfate, thus forming a  
 ferric hydroxide precipitate, to which was added  
 citric acid to form the ferric ammonium citrate. We

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intend to include ferric ammonium citrate made by any method, however. Likewise, the related, or derivative, as sometimes called herein, materials ferric butylamine citrate and ferric isopropylamine citrate are made in a similar manner, substituting butyl amine for the ammonium hydroxide or substituting isopropylamine for the ammonium hydroxide. In the case of isopropylamine, the designation "Fe IPA" in Table V means monoisopropylamine citrate and "Fe MIPA" means that the isopropylamine used to form the citrate was a mixture of monoisopropylamine, diisopropylamine, and triisopropylamine. Thus the term "ferric ammonium citrate or a lower alkyl substituted derivative thereof" is intended to include all versions of ferric ammonium citrate as described in the aforementioned Kruse and Mounce patent and those in which the ammonium moiety is substituted by amines having one, two or three alkyl groups, each having up to six carbon atoms. In each of the runs for which the results are shown in Table V, 3ml of a 67% solution of the designated phosphate ester gelling agent (Phosphate esters R, S, and T in Table V are similar to those used in Table I, all within the previously defined formula  $\text{HPO}_4\text{RR}'$ ) was mixed with a 3ml solution (100% active) of the ferric citrate shown in 300 ml of Diesel oil and gels were formed by stirring at low speed for two minutes. As is known in the art, the Marsh funnel test (last column) measures the time for 100 ml of the gel to discharge from a standard funnel.

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Table V

	Phosphate Ester	Citrate	Gel Eval	Formed (seconds)	Marsh (seconds)
5	R	Fe Amm	good	12	235
	S	Fe Amm	excel	17	291
	T	Fe Amm	excel	-	239
	R	Fe Bu Am	excel	13	94
	T	Fe Bu Am	excel	-	17
	S	Fe Bu Am	excel	-	7
10	R	Fe IPA	excel	27	18
	T	Fe IPA	excel	31	10
	S	Fe IPA	excel	24	6
	R	Fe MIPA	excel	16	78
	S	Fe MIPA	excel	44	6
15	T	Fe MIPA	excel	-	8

A further comparison of a phosphate ester gelled with ferric sulfate and the same phosphate ester gelled with ferric ammonium citrate showed the ferric ammonium citrate with a Fann 50 viscosity of 895-860 cps at 180°F while the ferric sulfate had a Fann 50 viscosity of 400-300 cps at 180°F.

In the following examples, a 50% ferric sulfate solution was used. About 14% by weight of the amine and about 14% by weight isopropanol were added to the ferric sulfate solution, with or without a polycarboxylic acid or an alkali metal salt thereof as indicated in the examples, to make an iron containing solution. Sufficient iron containing solution was then added to 300 ml Diesel oil containing about 0.3% phosphate ester to provide 0.6% of the iron containing solution in it, and the mixture was stirred and observed for the formation of a gel.

Example 11 -- various amines

	<u>gel time</u>
cyclohexylamine	1:20
butylamine	1:00 note -- Marsh funnel
	@ 1%: 11:27 min

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dicyclohexylamine	2:00
propylamine	2:00
morpholine	3:00

## 5        Example 12 -- polycarboxylic acid

Here 30g of the indicated polycarboxylic acid were added to 100g of a 50% ferric sulfate solution; the Diesel oil had 1% phosphate ester in it. Fe/Al means that one-fifth of the iron was replaced with aluminum.

10

gel time

Fe EDTA*	1:55
Fe citrate	1:27
Fe/Al EDTA*	1:00; Marsh 2:30
Fe/Al citrate	1:00; Marsh 1:34

15

\*Ethylene diamine tetraacetic acid

## Example 13 -- Amino Chelates

In these experiments, ammonium hydroxide or the indicated substitute (a molar equivalent to precipitate the  $\text{Fe}^{+3}$ ) was added to 100g of 50% ferric sulfate solution, and 30g of the chelant (citric acid or other polycarboxylic acid) was then added, followed by mixing; this was used to combine with the phosphate ester/Diesel oil mixture.

20

25

Ferric monoisopropanolamine citrate (FANN 50 @220F:

170  $\text{sec}^{-1}$ ; 385 cps

Ferric ammonium / nitrilotriacetic acid: gel formed

30        Ferric Ammonium Oxalate:        gel formed

Ferric Ammonium Gluconate:        gel formed

## Example 14 -- Chelates

35        The following results were obtained using 2% (based on

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the Diesel oil) iron chelates indicated mixed with 1% phosphate ester in Diesel oil:

gel

Diethylene triamine pentaacetic acid

5 (Formula II above): fair

Triamine tetraacetic acid of formula (III) above:

(Formula III above: good

Ferric gluconate: excellent

Ferric tartrate: excellent

10

Example 15 -- Alkanolamine Citrates

In these cases the ferric sources were made by first preparing 100g of a 50% solution of ferric sulfate, then adding the indicated amine and citric acid (both molar equivalents of the ferric iron). The resulting composition was stirred and added to Diesel oil containing 1% phosphate ester to provide 1% ferric iron in the oil. The results were as follows:

20

Monoethanolamine; Citric Acid excellent gel

Triethanolamine; Citric Acid Very good gel

Monoethanolamine; Citric Acid;

Partially neutralized phos ester very good gel

25

Triethanolamine; Citric Acid;

Partially neutralized phos ester excellent gel

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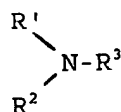
## Claims

- 5           1. Method of fracturing a subterranean formation comprising adding to a hydrocarbon liquid to be used as a fracturing fluid (a) about 0.3% to about 1.5% by weight, based on the hydrocarbon liquid, of an organic phosphate of the formula  $\text{HPO}_4\text{RR}'$  where R is a straight or branch chain alkyl, aryl, alkoxy or alkaryl group having from 6 to about 18 carbon atoms and R' is hydrogen or an aryl, alkaryl, alkoxy or alkyl group having from 1 to about 18 carbon atoms, and (b) a composition comprising (i) ferric iron in an amount sufficient to form a gel with said organic phosphate in said hydrocarbon liquid, and (ii) a polycarboxylic acid or an alkali metal salt thereof, having from 2-12 carbon atoms and up to three amine groups, and fracturing a subterranean formation with said hydrocarbon liquid.
- 10
- 15
- 20
- 25           2. Method of claim 1 wherein said composition (b) is added in an amount sufficient to provide 0.1 to 2.5 mole(s) of ferric iron for each mole of phosphate ester present in said hydrocarbon.
- 30           3. Method of claim 1 wherein said polycarboxylic acid or alkali metal salt thereof is present in a weight ratio of about 1:10 to about 10:1 to said ferric iron.



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4. Method of claim 1 wherein an amine of the formula

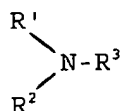


where R' is  $-(\text{CH}_2)_{2-6}\text{R}^4$ , R<sup>4</sup> is H or OH, R<sup>2</sup> is  $-(\text{CH}_2)_{0-6}\text{H}$  or  $-(\text{CH}_2)_{2-4}\text{OH}$ ,

R<sup>3</sup> is R<sup>2</sup> or  $-(\text{CH}_2)_{2-6}\text{N} \begin{array}{c} \text{R}_2 \\ \diagup \\ \text{R}^5 \end{array}$  and R<sup>5</sup> is R<sup>2</sup> or  $-(\text{CH}_2)_{2-6}\text{N} \begin{array}{c} \text{R}^2 \\ \diagup \\ \text{R}^2 \end{array}$

is also a part of composition (b), in a weight ratio to ferric iron of 1:10 to 10:1.

5. A composition for viscosifying a hydrocarbon containing a phosphate ester comprising (a) ferric iron (b) a polycarboxylic acid or alkali metal salt thereof having 2-12 carbon atoms and up to three amine groups in a weight ratio to said ferric iron of about 1:10 to about 10:1, and (c) an amine of the formula



where R' is  $-(\text{CH}_2)_{2-6}\text{R}^4$ , R<sup>4</sup> is H or OH, R<sup>2</sup> is  $-(\text{CH}_2)_{0-6}\text{H}$  or  $-(\text{CH}_2)_{2-4}\text{OH}$ ,

R<sup>3</sup> is R<sup>2</sup> or  $-(\text{CH}_2)_{2-6}\text{N} \begin{array}{c} \text{R}_2 \\ \diagup \\ \text{R}^5 \end{array}$  and R<sup>5</sup> is R<sup>2</sup> or  $-(\text{CH}_2)_{2-6}\text{N} \begin{array}{c} \text{R}^2 \\ \diagup \\ \text{R}^2 \end{array}$

in an amount up to about ten times by weight of the ferric iron.

6. Method of claim 1 wherein said polycarboxylic acid or alkali metal salt thereof is ethylene diamine tetraacetic acid or an alkali metal salt thereof.

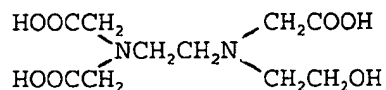
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7. Method of claim 1 wherein said polycarboxylic acid or alkali metal salt thereof is nitrilotriacetic acid or an alkali metal salt thereof.

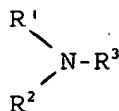
8. Method of claim 1 wherein said polycarboxylic acid or an alkali metal salt thereof is tartaric acid.

9. Method of claim 1 wherein said polycarboxylic acid or an alkali metal salt thereof is citric acid.

10. Method of claim 1 wherein said polycarboxylic acid as of the formula



11. A viscous fracturing fluid comprising a hydrocarbon liquid including about 0.3% to 1.5% by weight of an organic phosphate gelling agent, about 0.1 to about 2.5 mole(s) of ferric iron for each mole of phosphate gelling agent, a polycarboxylic acid or alkali metal salt thereof in a weight ratio of 1:10 to 10:1 to the ferric iron, and up to ten times the weight of the ferric iron of an amine of the formula



where  $\text{R}^1$  is  $(\text{CH}_2)_{2-6}\text{R}^4$ ,  $\text{R}^4$  is H or OH,  $\text{R}^2$  is  $(\text{CH}_2)_{0-6}\text{H}$  or  $(\text{CH}_2)_{2-4}\text{OH}$ ,

$\text{R}^3$  is  $\text{R}^2$  or  $(\text{CH}_2)_{2-6}\text{N} \begin{array}{c} \text{R}^2 \\ \diagup \quad \diagdown \\ \text{R}^5 \end{array}$  and  $\text{R}^5$  is  $\text{R}^2$  or  $-(\text{CH}_2)_{2-6}\text{N} \begin{array}{c} \text{R}^2 \\ \diagup \quad \diagdown \\ \text{R}^2 \end{array}$

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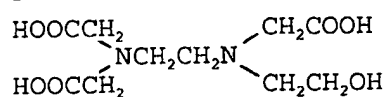
12. Composition of claim 5 wherein said polycarboxylic acid or alkali metal salt thereof is ethylene diamine tetraacetic acid or an alkali metal salt thereof.

13. Composition of claim 5 wherein said polycarboxylic acid or alkali metal salt thereof is nitrilotriacetic acid or an alkali metal salt thereof.

14. Composition of claim 5 wherein said polycarboxylic acid or alkali metal salt thereof is tartaric acid.

15. Composition of claim 5 wherein said polycarboxylic acid or alkali metal salt thereof is citric acid.

16. Fracturing fluid of claim 11 wherein said polycarboxylic acid is of the formula



17. Fracturing fluid of claim 11 wherein said polycarboxylic acid or alkali metal salt thereof is ethylene diamine tetraacetic acid or an alkali metal salt thereof.

18. Fracturing fluid of claim 11 wherein said polycarboxylic acid or alkali metal salt thereof is nitrilotriacetic acid.

19. Fracturing fluid of claim 11 wherein said polycarboxylic acid or alkali metal salt thereof is tartaric acid.

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20. Fracturing fluid of claim 11 wherein said polycarboxylic acid or alkali metal salt thereof is citric acid.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US97/19411

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(6) : C09K 3/00; E21B 43/26 US CL : 507/238,922; 166/308 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 507/238,922; 166/308  Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched NONE  Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) NONE		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,514,645 A [MCCABE et al] 07 May 1996, see entire document.	1-20
A	US 4,153,649 A [GRIFFIN JR.] 08 May 1979, see entire document.	1-20
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
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Date of the actual completion of the international search 13 MARCH 1998	Date of mailing of the international search report 09 APR 1998	
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer <i>Debbie Thomas</i> DAVID M BRUNSMAN Telephone No. (703) 308-6661	